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WELDING AND BRAZING OF MOLYBDENUM

DEFENSE METALS INFORMATION CENTER
Battelle Memorial Institute
Columbus 1, Ohio

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WELDING AND BRAZING OF MOLYBDENUM

by

N. E. Weare and R. E. Monroe

to

OFFICE OF THE DIRECTOR OF DEFENSE RESEARCH AND ENGINEERING

DEFENSE METALS INFORMATION CENTER
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WELDING AND BRAZING OF MOLYBDENUM

SUMMARY

Molybdenum can be welded to itself by any of several methods. The most widely studied and most adaptable methods are inert-gas-shielded arc welding and brazing. Resistance welding ultrasonic welding, pressure welding, and similar processes also are used on molybdenum. These latter processes do not lend themselves readily to the joining of complex structures, and the properties of joints made by these methods may leave much to be desired.

To obtain the most useful molybdenum joints, the following considerations should be remembered.

(1) Minute quantities of oxygen, nitrogen, and carbon greatly lower the ductility of molybdenum. This effect is a problem to be kept in mind particularly when fusion welding molybdenum. Contamination can occur from residuals in the base metal, from the surface of the weldment, or from the welding atmosphere.

(2) The extent of fused or recrystallized zones in molybdenum should be kept to a minimum in fusion welding and recrystallized zones should be avoided, if possible, when brazing. These zones are very sensitive to embrittlement by residual oxygen, nitrogen, or carbon. Recrystallization also greatly lowers the strength of wrought molybdenum.

(3) Molybdenum possesses a transition temperature typical of body-centered cubic metals. At room temperature, molybdenum may be brittle, but at temperatures slightly above this molybdenum exhibits sufficient ductility to be formed.

(4) Molybdenum is highly notch sensitive, and stress raisers should be avoided in molybdenum joints.

(5) The use of brazing filler metals that alloy with molybdenum to form brittle intermetallics, low-melting eutectics, or alloys in the molybdenum with low recrystallization temperatures should be avoided if molybdenum is to be brazed for structural use at elevated temperatures.

INTRODUCTION

In recent years, there has been an emphasis on the application of molybdenum as a structural material for use at high temperatures. This has been brought about by the future material requirements in the aircraft, missile, jet-engine, and nuclear-reactor fields. In order to utilize fully the unique properties of molybdenum, methods must be found to join molybdenum to itself and to other heat-resisting materials. For some years, the problem of producing ductile joints in molybdenum has been studied. In preparing this report, it was felt that only data obtained during the last 5 or 6 years are of value, because of the improvements in purity over that of commercial molybdenum produced prior to this time. During the past few years, there has been a noticeable improvement in the ductility of fusion welds in molybdenum, which can be directly related to improvements in the commercially produced metal.

This report covers most of the published work on joining molybdenum to itself. The metallurgical considerations involved in joining molybdenum are discussed, as well as testing, cleaning, and joining procedures. A survey of the published literature reveals considerable information of value to designers and materials and process engineers associated with the defense industry, although only a limited amount of this information has been reported as standardized engineering data.

METALLURGICAL CONSIDERATIONS

When joining molybdenum, there are certain metallurgical considerations that must be kept in mind. These include: (1) type of molybdenum, (2) microstructure, (3) impurities, (4) alloying elements, (5) physical properties, and (6) notches. Successful fabrication and joining of molybdenum is largely governed by these basic metallurgical factors.

Types of Molybdenum

Molybdenum and molybdenum-base alloys are available commercially in two types – one produced by powder-metallurgy techniques and another produced by arc casting. Arc-cast molybdenum has the advantage of higher density, larger ingot size, and lower gas content. Fusion welds in arc-cast material can be made without cracks and porosity. This is not true of most powder-metallurgy alloys, although a recent patent has been issued for a weldable powder-metallurgy alloy containing a small percentage of titanium.(12)* The primary reason for the improved fusion-welding

*References given at end of this report.

characteristics of arc-cast molybdenum is its exceptionally low gas content, especially oxygen. The approximate amounts of impurity elements, oxygen, nitrogen, and carbon, are given in Table 1 for both types of molybdenum.[2,5,18] Powder-metallurgy molybdenum can be joined by solid-state bonding or by brazing without porosity formation provided it is not heated to temperatures near its melting point.[3]

TABLE 1. OXYGEN, NITROGEN, AND CARBON ANALYSES OF MOLYBDENUM[2,5,18]

Type of Molybdenum	Composition, weight per cent Oxygen	Nitrogen	Carbon
Commercial powder metallurgy	0.0005-0.0071	0.0001-0.004	0.003-0.005
Commercial arc cast	0.0002-0.0022	0.0001-0.0002	0.010-0.030

Since around 1953 there has been a steady increase in the ductility of molybdenum fusion welds. This has been primarily due to improvements in the quality of commercial molybdenum. Improvements in arc-casting technique have steadily lowered the amount of residual carbon in molybdenum ingots and still maintained low percentages of oxygen and nitrogen.

Considerable research effort has also gone into determining methods of producing ultra-high-purity molybdenum. These efforts have shown high-purity molybdenum to be very ductile when compared with commercial-purity molybdenum. However, such high-purity molybdenum is not now commercially available and is not discussed in this report.

Microstructure

The microstructure of molybdenum has considerable influence on its strength and ductility. Molybdenum receives its strength through strain hardening; therefore, it is desirable to keep molybdenum in the wrought condition. Not only does recrystallization of wrought molybdenum lower its strength, but it may result in embrittlement by the impurities present in commercial alloys, since the tolerance for impurities decreases as the grain size increases. Impurities have much less effect on wrought molybdenum because of its fibered grain structure. Working of molybdenum breaks up the grain-boundary films that cause brittle failure through the grain boundaries. Recrystallization raises the ductile-to-brittle transition temperature because a given amount of impurity element can form a more continuous network of grain-boundary films in the recrystallized structure having large

grains. Fusion welds in molybdenum contain a coarse-grain structure in the weld metal and a coarse-grained recrystallized structure in the heat-affected zone. For this reason, the weld metal and the heat-affected zone in molybdenum are less ductile than base material of the same composition.

Increasing grain size also broadens the temperature range in which completely brittle to completely ductile behavior is obtained.[17] This is illustrated in Figure 1. The temperature range is relatively narrow for wrought molybdenum (the lower graphs). Larger weld-metal grains increase the transition range and transition temperature (middle graphs). The very large-grain cast material has an extremely wide transition range and an even higher transition temperature. Contamination may have played a role in decreasing the ductility and increasing the breadth of the transition-temperature range of the welded samples.

When joining by brazing or solid-state bonding, temperatures and time should be held below the required minimum for recrystallization. The reported minimum temperatures for recrystallization in 1 hour for materials previously reduced 97 per cent at 2200 to 1900 F are as follows:[2]

Unalloyed molybdenum - 2150 F

Molybdenum-0.3 per cent niobium - 2200 F

Molybdenum-0.5 per cent titanium - 2450 F

Molybdenum-1 per cent vanadium - 2150 F

The maximum temperature that can be tolerated without causing any detrimental effects associated with recrystallization may be higher or lower than the above values and should be determined experimentally. The prior history of each material should be studied carefully to determine the proper time-temperature cycle for brazing or solid-state welding operations. The above tabulation shows the alloy containing titanium to have the highest recrystallization temperature and, for this reason, it is receiving much attention at the present time.

Impurities

Oxygen, nitrogen, and carbon are the most common impurity elements that remain in commercial molybdenum. The effects of these impurities on the ductility of molybdenum have been determined by studying the ductile-to-brittle transition temperature of cast molybdenum.[1] The results of this study are shown in Figure 2. As can be seen from this figure, extremely small percentages of oxygen have a great embrittling effect on cast molybdenum. Nitrogen and carbon have much less effect on ductility than does oxygen. Embrittlement occurs when the oxides, nitrides, or carbides form

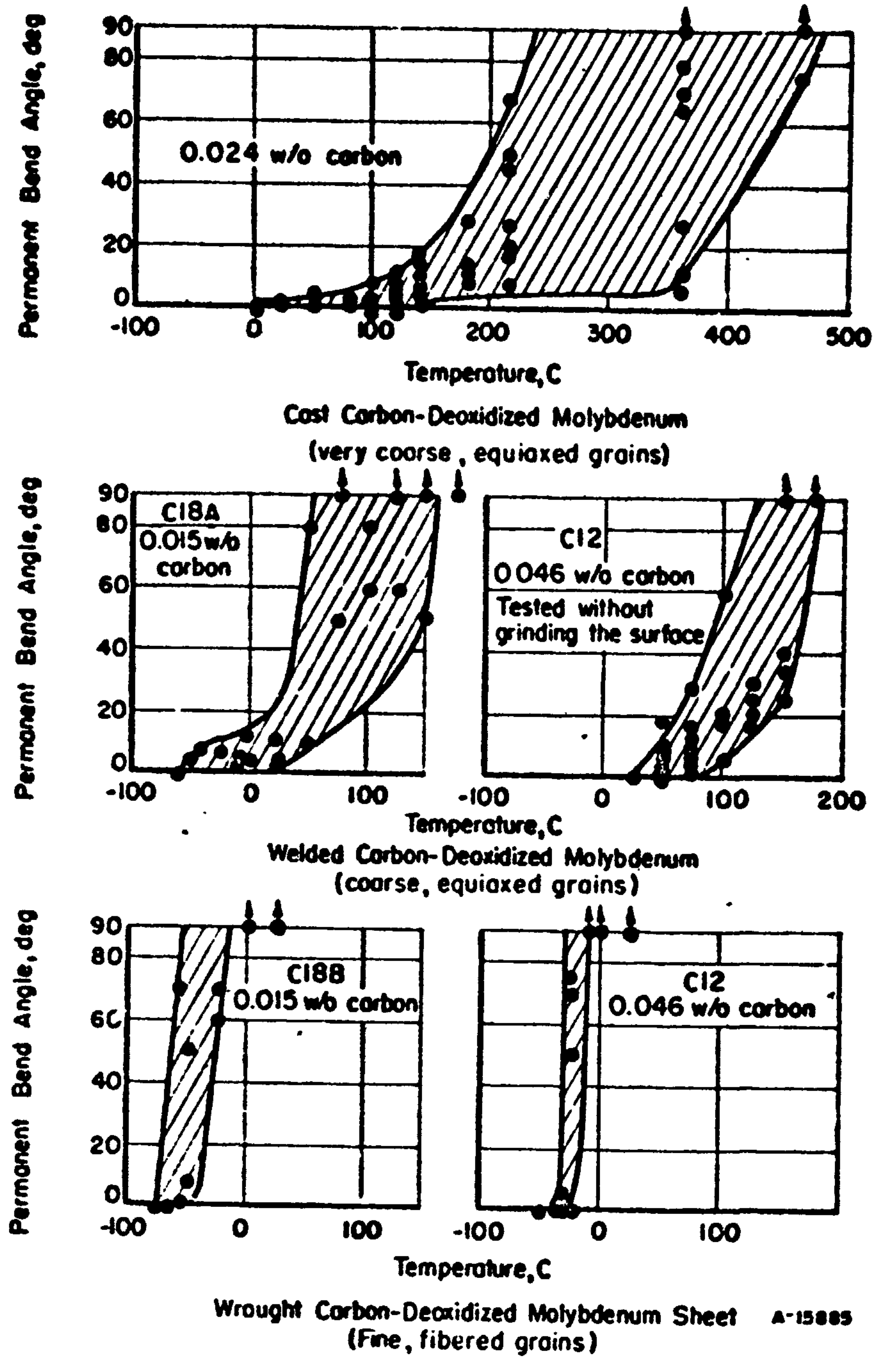

FIGURE 1. TRANSITION TEMPERATURES AND RANGES OF MOLYBDENUM WITH VARIOUS GRAIN SIZES(17)

From bend tests at 0.016 in. /in. /sec strain rate.

a grain-boundary film, thus causing failure to occur intergranularly.[1,13,35] Grain-boundary films form upon cooling from the melting point or from high temperatures because of the decreasing solubility of these elements as temperature decreases.

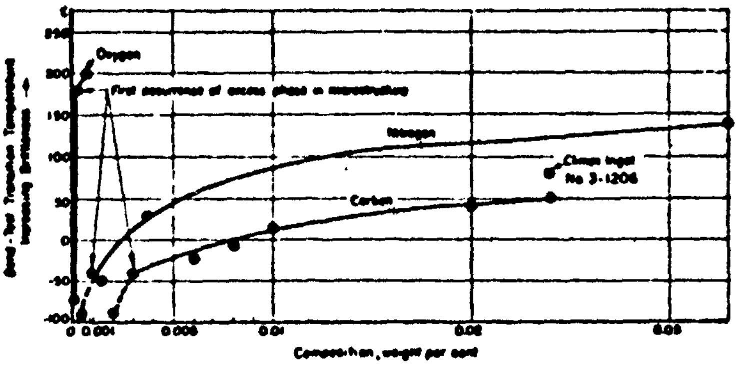

FIGURE 2. EFFECTS OF OXYGEN, NITROGEN, AND CARBON UPON BRITTLE TRANSITION TEMPERATURE OF CAST MOLYBDENUM[1]

From bend tests at 0.038 in./in./sec strain rate.

Some relationships between the amounts of oxygen and nitrogen and ductility have been found for molybdenum fusion weldments.[11,13,14] These effects were studied by adding oxygen or nitrogen to an argon welding atmosphere. Figures 2, 3, and 4 indicate that impurities have somewhat less effect on the ductility of fusion weldment than they do on cast molybdenum. However, direct comparisions of the results of these two studies are not possible because of: (1) differences in base materials to which the additions were made, (2) grain size, and (3) strain rate. The same results for fusion weldments are discussed in the section on Fusion Welding, but the results are discussed in relation to impurities in the welding atmosphere.

Hydrogen embrittlement in molybdenum does not occur. In the above-mentioned study of cast molybdenum, the investigators found that ingots melted under partial pressure of hydrogen did not pick up additional hydrogen.[1] Diffusion of hydrogen through molybdenum is not perceptible at elevated temperatures. For this reason, molybdenum is used as a barrier against hydrogen diffusion in certain types of apparatus. Hydrogen contamination is, therefore, not a problem when joining molybdenum by any of the processes to be discussed. Metallic impurities are present in only minor amounts and apparently have no noticeable effect on the ductility of molybdenum. One study has shown that contamination by tungsten that may occur in tungsten arc welding lowers the ductility of molybdenum welds slightly.[15]

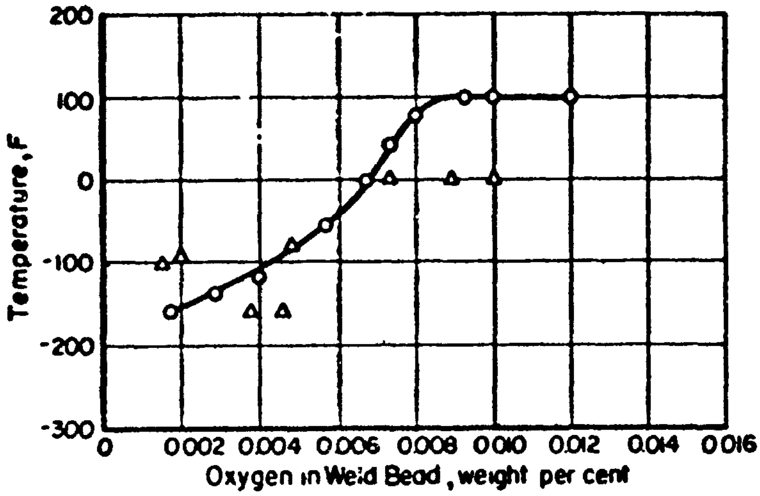

FIGURE 3. RELATIONSHIP BETWEEN OXYGEN IN THE WELD BEAD AND THE BRITTLE-FAILURE TEMPERATURE(13)

From bend tests at 0.0003 in./in./sec strain rate.

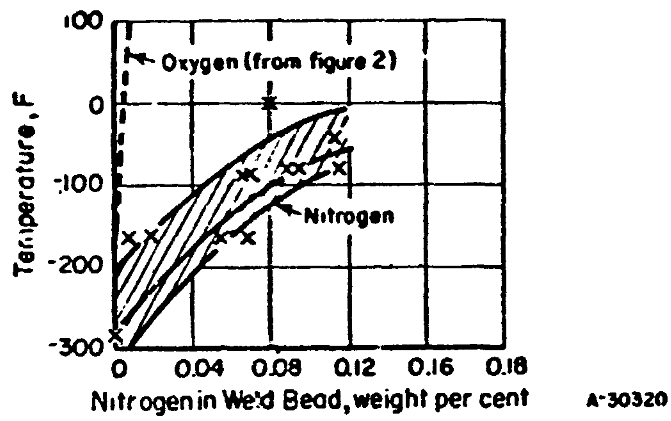

FIGURE 4. RELATIONSHIP BETWEEN NITROGEN IN THE WELD BEND AND THE BRITTLE-FAILURE TEMPERATURE(14)

From bend tests at 0.0003 in./in./sec strain rate.

Alloying Elements

Many investigators have concentrated their efforts on determining the effects of small additions of alloying elements on the ductility of molybdenum. These additions have been made with the idea of overcoming the deleterious effects of oxygen on ductility. Work at Battelle Memorial Institute has centered on studies of additions to cast molybdenum to overcome the effects of oxygen.(1) The Battelle investigators found that additions of titanium in the range of 0.5 to 1.0 weight per cent improved the ductility of cast molybdenum. This is illustrated in Figure 5. Research at Climax Molybdenum Company also has shown an improvement in ductility of molybdenum with small additions of titanium and/or zirconium.(4) Additions of titanium raised the recrystallization temperature of wrought molybdenum and, in this manner, also reduced the possibility of embrittlement.

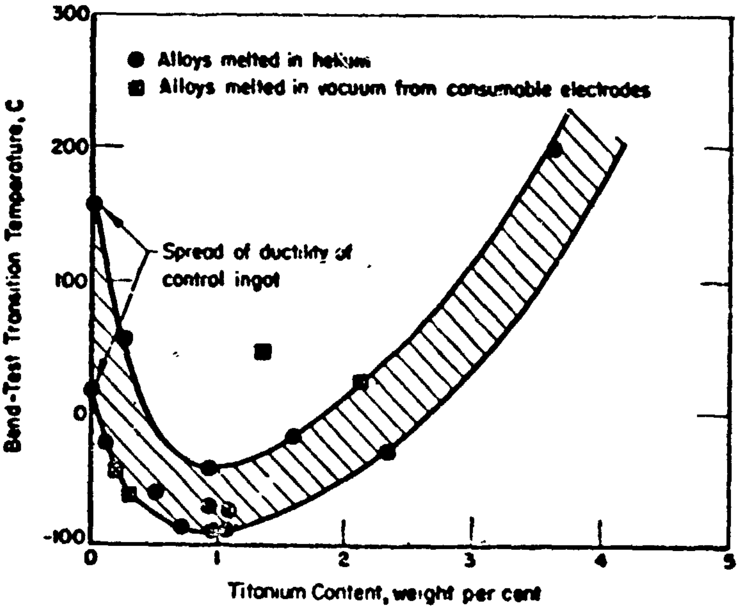

FIGURE 5. EFFECT OF TITANIUM ON TRANSITION TEMPERATURE OF CAST MOLYBDENUM

From bend tests at 0.038 in./in./sec strain rate.

Alloying of molybdenum to overcome the deleterious effects of oxygen on fusion welds offers promise in improving the ductility of welds in molybdenum. Titanium presently appears to be the most promising alloying element for this purpose. Monroe, Weare, and Martin found a relationship similar to that shown in Figure 5 for welds and alloys prepared from purified molybdenum.(17) Weldments containing 0.7 weight per cent titanium had the

lowest brittle-to-ductile transition temperature. However, the ductility of welds produced by these investigators in unalloyed arc-cast carbon-deoxidized molybdenum that was available in 1954 was comparable with the ductility of welds in the high-purity molybdenum-titanium alloys. A commercial arc-cast carbon-deoxidized alloy is now available that contains a nominal 0.5 per cent titanium.

Platte found the most ductility in molybdenum weldments in the commercial arc-cast alloy containing 0.46 per cent titanium and 0.05 per cent carbon.[20] Tungsten-arc welds in this alloy were ductile at room temperature, as determined by a slow-bend test. Monroe, Weare, and Martin found no improvement in weldment ductility over unalloyed material in a similar commercial alloy containing 0.46 per cent titanium and 0.029 per cent carbon.[17] In the above-mentioned study by Platte, it also was determined that aluminum lowers the temperature for ductile behavior in a slow-bend test but caused porosity in tungsten-arc welds.

It was also surmised during Platte's study on the basis of the carbon contents in several different heats of material that an increased carbon content from 0.02 to 0.06 per cent increased weldment ductility.[21] This is completely opposite the result obtained by Monroe, et al., who found increased ductility with decreasing carbon content from commercially fabricated molybdenum in heats ranging from 0.015 to 0.042 per cent carbon.[17] Another study by these investigators indicated significant differences in the ductilities of weldments in different lots of arc-cast molybdenum of about the same carbon content. This seemed to indicate some effect of sheet-fabrication history on weldment ductility.[15] The effect of carbon on weldment ductility has not been resolved, and could be determined only by a controlled experiment in which several carbon contents were studied and all sheet material was fabricated in an identical manner. In unalloyed molybdenum, it is beneficial to have some carbon present to react with residual oxygen in welding atmospheres to produce a deoxidizing effect.

Improvements in fusion-weldment ductility have been made by some investigators by the use of a 55 weight per cent molybdenum-45 weight per cent rhenium filler-metal composition.[26] The filler wire was made by winding rhenium wire around the molybdenum wire. Transverse bend radii of 3T were obtained at room temperature, which represents a significant improvement over the 6T radii obtained when molybdenum filler was used. Molybdenum-rhenium alloys of the composition given are ductile.

Physical Properties

The thermal conductivity and thermal expansion are important factors to be considered in brazing molybdenum. The coefficient of thermal conductivity for molybdenum is very high at room temperature, 70 Btu/sq ft/ft/hr/°F, and this drops slowly as the temperature is increased to 2100 F,

where the value is 56.5 Btu/sq ft/ft/hr/°F.[6] These high coefficients of thermal conductivity permit rapid heating and a minimum of time at the brazing temperature, thereby minimizing the danger of uneven heating. The thermal expansion of molybdenum is low compared with that of most metals, the mean thermal expansion coefficient in the temperature range from 32 to 2200 F being only 3.8×10^{-6} in./in./°F. Failure to design properly for this low value of thermal expansion can lead to trouble when molybdenum is brazed to other metals that may have thermal expansion coefficients three or four times higher.

Notches

All joints in molybdenum should be designed to avoid notch effects at the joints. Weare, Monroe, and Martin have showed longitudinal weld cracking to result when a notch remained at the root of a butt weld because of incomplete penetration.[18] Longitudinal cracks also can occur with complete penetration if a notch is left at the start or end of a weld. Transverse cracking occurred in weld metal and propagated into the base metal if reduced weld cross-sectional areas occurred. Platte experienced severe crater cracking in many weldments because of the notch remaining as a result of shrinkage during solidification.[20] The geometry of the specimen used by Platte produced a high stress at this notch. In welding molybdenum, steps should be taken to eliminate craters at the ends of fusion welds.

Jacobson and Martin found it impossible to avoid tensile failure through recrystallized base metal at low loads in brazed double-shear lap joints.[41] Redesign of the joint to minimize the notch effect still did not prevent this type of failure at room temperature. Detrimental effects from joint notches on assemblies that are not recrystallized during brazing also would be expected. Olds and Fisher demonstrated that molybdenum in the fibered condition is notch sensitive in bending.[7] The presence of a notch surrounding resistance or ultrasonic spot welds probably contributes to the low strength and the brittleness of these joints

TESTING OF JOINTS

Ductility is a property of primary interest when testing joints in molybdenum. Fusion-weld ductility is normally determined by a bend test. Most researchers have used the transverse bend test, since this indicates the ductility in the least ductile direction for a fusion weld due to weld-metal grain orientation. A transverse bend specimen is illustrated in Figure 6. In this test, the greatest amount of deformation generally occurs in the heat-affected zone, although the greatest stress is at the centerline of the weld. Fracture nearly always occurs in the weld metal. For comparison purposes,

the ductilities of various welds can be determined in various manners. Some investigators measure the total deflection during testing.[11] This measures both elastic and plastic deformation. Other investigators determine the plastic deformation by measuring the permanent bend angle after fracture.[17] Still others use a transverse guided-bend test.[27] In this test, the weldment is made to conform to the radius of the punch. Some investigators use the longitudinal bend test (Figure 6), since weld, heat-affected zone, and base metal must undergo the same strain during bending. The constant-moment bend test has been used by some investigators to determine the ductility of upset welds in molybdenum.[36,37] This test indicates whether the weld or heat-affected zones were ductile or brittle. Also shown in Figure 6 is a tensile or stress-rupture test specimen for fusion welds in molybdenum sheet.[27]

For the purpose of comparing weldments made in different lots or alloys of molybdenum or welds made in different welding atmospheres, investigators have used several methods. The three for which the greatest amount of data are presently available are:

(1) Determination of the ductile-to-brittle transition temperature[11,17]

(2) Determination of the temperature of ductile failure for the test (an arbitrary value, usually the limit of the test equipment)

(3) Determination of the room-temperature ductility.[15]

When attempting to compare the results of studies carried out by different investigators, it must be kept in mind that strain rate has an effect on the ductility of molybdenum. This effect is shown in Figure 7.[9] Transition temperatures are increased as strain rate increases, primarily because of an increase in the temperature range in which the yield strength increases rapidly (Figure 7). Relatively small changes in strain rate can shift the fracture behavior from ductile to brittle at room temperature.

Resistance and ultrasonic spot welds have been tested by tension-shear and cross-tension tests. Upset butt welds, flash welds, and brazed butt joints have been tension tested to determine strength, elongation, and reduction in area.

All molybdenum weldments should have their surfaces ground to produce a smooth surface for testing. Surface grinding removes any microcracks or reduced cross-sectional areas that would tend to produce brittle failures. The removal of surface defects allows better comparisons to be made of different weldments. Battelle investigators found an improvement in fusion-weldment ductility when the molybdenum weldment surfaces had been ground.[17] In testing upset or flash welds, the upset or flash must be removed in order to test the weld properly.

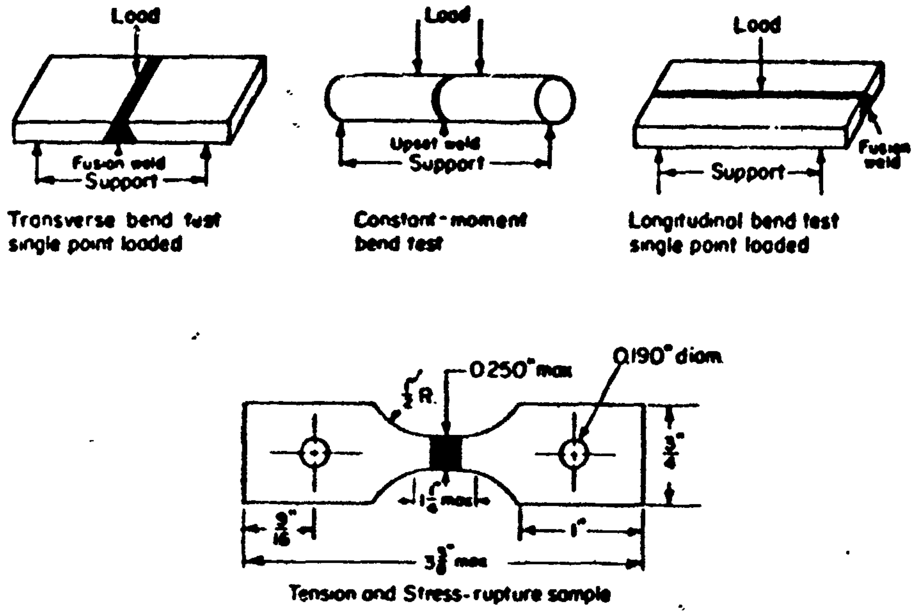

FIGURE 6. TEST SPECIMENS FOR FUSION OR UPSET WELDS IN MOLYBDENUM

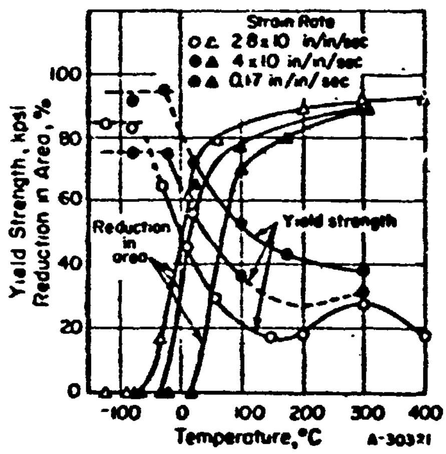

FIGURE 7. EFFECT OF TEMPERATURE AND STRAIN RATE ON DUCTILITY, YIELD STRENGTH, AND BRITTLE-FRACTURE STRENGTH OF ANNEALED MOLYBDENUM

Grain size 900 grains/sq mm. (19)

Since the shear strength of lap-brazed joints is important, double-lap shear specimens and slotted specimens have been used to study the shear strength of brazed joints.[41] Tensile tests of brazed butt joints also have been performed.[42] These test specimens are shown in Figure 8. Because of the notch effect present in the specimens for shear testing, the determination of the room-temperature shear strengths has not been possible. However, successful short-time tests have been carried out at 1800 F.[41]

CLEANING PROCEDURES

The removal of surface films from molybdenum before joining by any method is mandatory. Cleaning should be done immediately before joining, when possible. There are several methods that will clean molybdenum satisfactorily for joining. Mechanical means of removing oxide, such as sandblasting, vapor blasting, or abrasion, are acceptable methods of oxide removal, but can be used only on simple parts. Oxide removal by chemical means is a more satisfactory method of cleaning molybdenum, especially if complex shapes are involved.

The removal of heavy oxides from molybdenum is most easily accomplished by immersion in a molten salt bath. Two fused-salt compositions used are:

(1) 70 per cent NaOH and 30 per cent $NaNO_2$ operating at 500 to 700 F[10]

(2) Commercial Martempering salt, consisting of a mixture of sodium and potassium nitrites and nitrates operating at 700 F.[17]

The first bath requires close control because the molten salt attacks the molybdenum. No gross attack was noted when using the second bath. Salt-bath cleaning should be followed by another treatment to remove light oxide films before joining.

Electrolytic etchants may be used to remove surface oxides, but are not always satisfactory for cleaning complex shapes. In all cases studied, the molybdenum was severely attacked at the grain boundaries.

The most popular method employed in cleaning molybdenum for joining involves the use of chemical etchants. Many of these etchants attack the molybdenum, but if the time of immersion in the solution is controlled, all can be used satisfactorily. Three cleaning methods used successfully are:

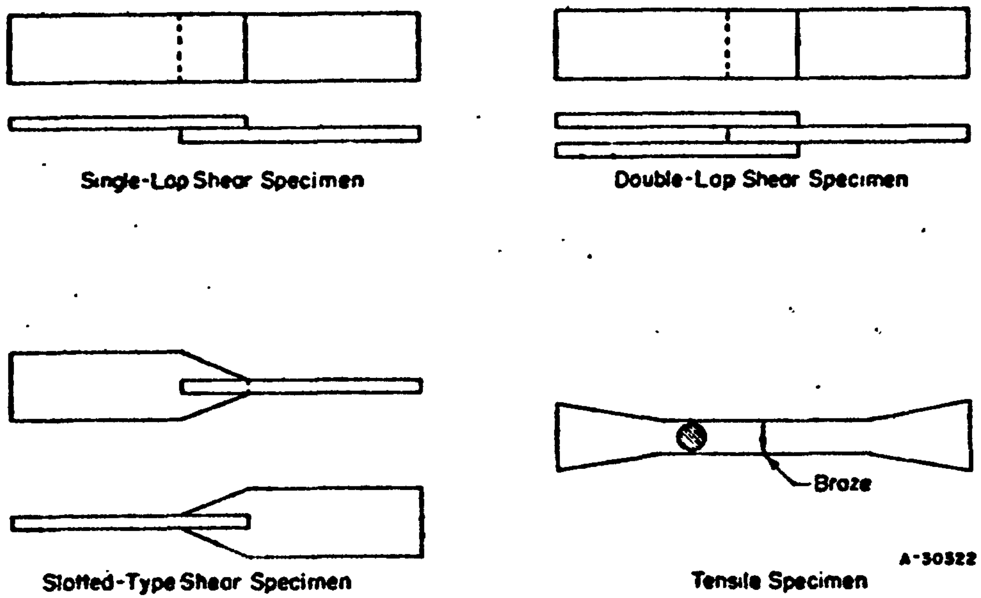

FIGURE 8. SPECIMENS FOR TESTING BRAZED JOINTS

(1) Immersion in a glass-cleaning etch composed of 95 per cent H_2SO_4, 4.5 per cent HNO_3, 0.5 per cent HF, and 18.8 g/l Cr_2O_3, operating at 120 to 140 F. This etchant has been used with a great deal of success for cleaning molybdenum for welding and brazing.[15,17,18]

(2) A recently suggested two-step treatment:[10]

(a) Immersion in an alkaline bath consisting of of 10 per cent NaOH, 5 per cent $KMnO_4$, and 85 per cent H_2O, by weight, operating at 150 to 180 F, 5- to 10-minute immersion time.

(b) Immersion for 5 to 10 minutes in a bath to remove the smut resulting from the first treatment. The second bath consists of 15 per cent H_2SO_4, 15 per cent HCl, 70 per cent H_2O, plus 6 to 10 weight per cent per unit volume chromic acid.

(3) A nine-step procedure to prepare molybdenum-0.5 per cent titanium alloy for welding:[27]

(a) Degrease 10 minutes in trichloroethylene vapor degreaser.

(b) Immerse in alkaline cleaner for 2 to 3 minutes (commercial cleaner).

(c) Rinse in cold water.

(d) Buff and vapor blast.

(e) Immerse in alkaline cleaner (same as b).

(f) Rinse.

(g) Electropolish with 8- to 12-ampere current in a bath of 80 per cent H_2SO_4 at 130 F.

(h) Rinse in cold water.

(i) Wrap each piece in a clean paper towel.

Molybdenum dioxide can be reduced by hydrogen with a dew point of 80 F when heated above 600 F.[43] This is of importance for brazing operations, although precleaning is recommended. Grease or fingerprints can be removed by scrubbing under a solvent such as acetone or by vapor degreasing.

JOINING PROCESSES

Molybdenum can be joined by several methods. These methods can be divided into four general classifications - fusion welding, resistance welding, solid-state welding, and brazing. The joining of molybdenum by these methods is discussed in the following sections.

Fusion Welding

Fusion welding is one of the most widely used methods of joining molybdenum. Studies have made using the inert-gas-shielded tungsten-arc and consumable-electrode processes, submerged-arc welding, atomic hydrogen, and, recently, the electron-beam processes. Of these processes, the tungsten-arc process has been used most extensively and will be discussed in the greatest detail. Several organizations have fabricated molybdenum assemblies by using the tungsten-arc process.

Since the development of the inert-gas-shielded arc-welding process, atomic-hydrogen welding of molybdenum has not been used extensively. For this reason, discussions of this process are not included in this report. Inert-gas-shielded welding of molybdenum can be carried out with a nonconsumable or a consumable electrode. Heat for fusion for the nonconsumable-electrode welding process is provided between a tungsten electrode and the metal being welded. Filler metal is added directly to the molten weld pool. When a consumable electrode is employed, the arc is maintained between the workpiece and a molybdenum electrode. The molybdenum electrode is consumed and filler metal is propelled through the arc to the weld joint. Brief investigations have been made to study submerged-arc welding of molybdenum, and presently molybdenum is being welded using an electron beam. These processes will be discussed briefly.

Assuming that the molybdenum has been sufficiently cleaned prior to welding, the major source of contamination is the welding atmosphere. Considerable research has been conducted to determine quantitatively the effects of atmospheric contaminants on the ductility of molybdenum weldments. Platte determined the effects of additions of oxygen and/or nitrogen to the welding atmosphere on the bend-test ductile-brittle transition temperature.[13,14] The results of these studies are shown in Figures 9 and 10. He also established a relationship between oxygen in the atmosphere and the occurrence of centerbead cracking in fusion welds.[13] He found that if 0.2 per cent or more oxygen were present in the welding atmosphere, cracking would occur in welds in 1/16-inch-thick unalloyed arc-cast molybdenum. This cracking might not have occurred in alloyed molybdenum, and the results of these studies were dependent upon the degree of weld restraint provided by the bead-on-plate specimens used. Nitrogen in the welding atmosphere was found to have less effect on weldment ductility, and additions of

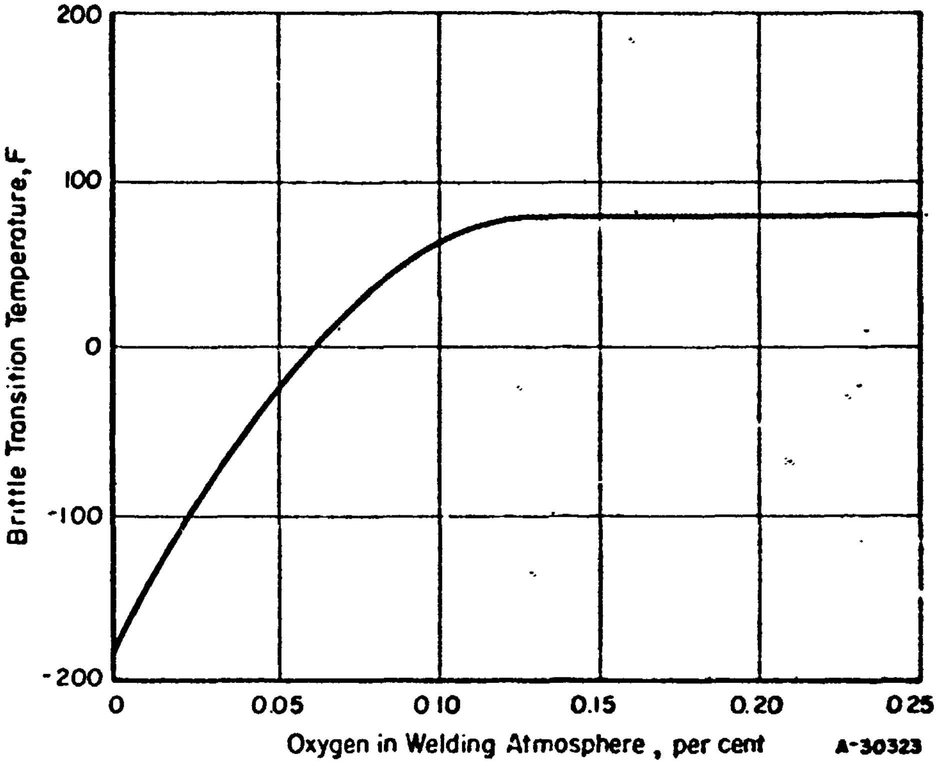

FIGURE 9. EFFECT OF OXYGEN IN WELDING ATMOSPHERE ON BRITTLE TRANSITION TEMPERATURE OF WELDS(13)

From bend tests at 0.0003 in./in./sec strain rate.

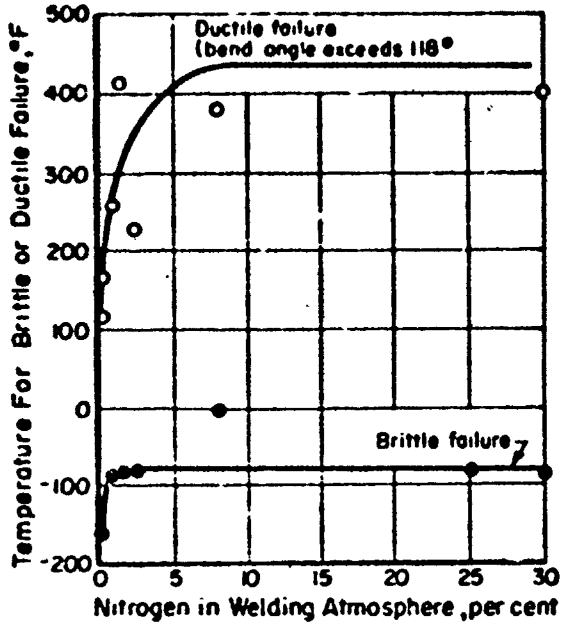

FIGURE 10. EFFECT OF NITROGEN IN THE WELDING ATMOSPHERE ON THE TEMPERATURE FOR BRITTLE AND DUCTILE FAILURE FOR FUSION WELDS IN 0.062-INCH-THICK MOLYBDENUM

From bend test at 0.0003 in./in./sec strain rate.[14]

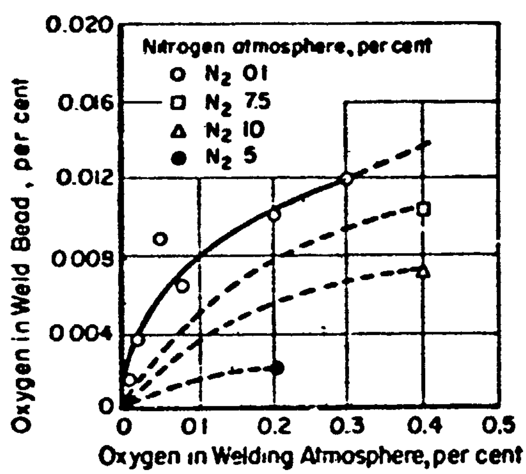

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FIGURE 11. OXYGEN ACQUIRED DURING WELDING AS A FUNCTION OF OXYGEN AND NITROGEN IN THE WELDING ATMOSPHERE[14]

up to 50 per cent nitrogen to the welding atmosphere did not cause hot cracking.[14] This same study also indicated an interaction between oxygen and nitrogen in the welding atmosphere that reduced the pickup of oxygen to some degree. This is illustrated in Figure 11. However, the addition of nitrogen to the welding atmosphere to lessen the pickup of oxygen does not improve the weldment ductility over that of welds made in pure inert atmosphere.

Weare, Monroe, and Martin studied the effect of ultimate vacuum obtained in vacuum purging a dry box prior to welding molybdenum.[15] They found the ductility of welds to be decreased when the dry box was evacuated to 100 microns of mercury, rather than the 0.1 micron normally used in their studies. Average room-temperature bend angles of 28 and 42 degrees were found when the chamber was purged to 100 and 0.1 micron of mercury, respectively. They also made several welds outside the dry box using various shielding devices. These welds were not so ductile, nor was ductility so consistent, as for welds made in the dry box.

Some investigators believe that the shielding gas used for welding molybdenum must be purified prior to use.[13] However, shielding gases are available in high purities, and purifying trains may not lower the amount of impurities present sufficiently to justify their use. There are several methods of drying and purifying gases for welding molybdenum. The system used by Platte is shown in Figure 12. Here, argon is supplied in tank form with a guaranteed minimum purity of 99.995 per cent and helium is supplied with a purity exceeding this value.[16] Purification of the gas, once a dry box has been filled with the shielding gas, probably is beneficial, since it will remove residual contaminants and absorbed and adsorbed gases released when welding. This can be accomplished by welding on titanium or zirconium for several minutes before welding molybdenum.[17] Either argon

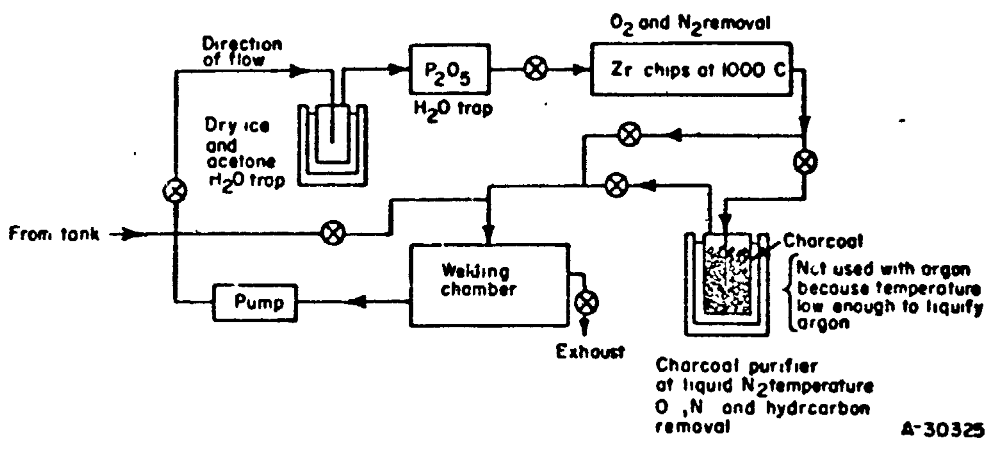


FIGURE 12. WELDING – ATMOSPHERE – PURIFICATION SYSTEM[20]

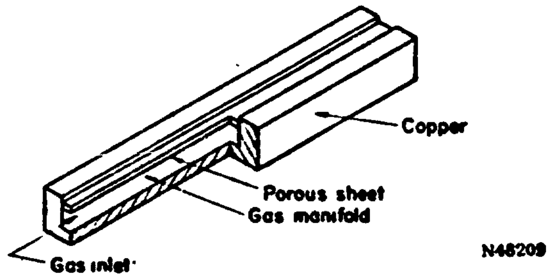
or helium may be used to shield molybdenum during welding. Helium is preferred by many because of the greater heat available for fusing the molybdenum.[15,17,18] The only method of determining whether shielding is adequate for welding molybdenum is to make sample welds for testing. Lack of discoloration of molybdenum weldments is no sign they have not become embrittled by contaminants.

It has been known for some time that, if adequate shielding is used, ductile welds can be made in high-purity molybdenum. Johnston, Udin, and Wulff reported some ductility of fusion welds made in high-purity molybdenum (0.01 per cent carbon, 0.001 per cent oxygen) prepared by the hydrogen reduction of molybdenum pentachloride when only brittle welds could be produced in commercial molybdenum available at the time of their study.[35]

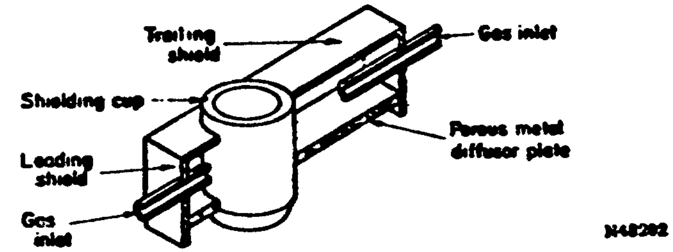
Various studies have indicated that molybdenum welds should be made in a dry box to insure the best shielding. This is almost mandatory when welds must be made manually. Both vacuum-purged and flow-purged dry boxes have been used successfully. However, welds can be made outside dry boxes, providing adequate shielding is provided. It has been shown that welds with some ductility could be made using either standard shielding cups or leading-trailing shields in conjunction with a gas backup.[15] Shields must provide shielding for all areas heated above a temperature at which oxides form on the unwelded molybdenum. Several types of shield used in conjunction with a shielding cup and gas backup are shown in Figure 13.[19] All gas lines and shield parts should be dried before welding to prevent moisture pickup by the shielding gas. Sufficient purging time also must be provided for each shield to remove entrapped air. These shields should be used as close to the weld as possible, and proper shielding-gas flows should be maintained. Surface oxidation of a completed molybdenum weld does not appear to have an effect on the ductility of the weld.

Porosity was noted by Weare, Monroe, and Martin along the fusion line of many tungsten-arc butt welds in arc-cast molybdenum.[15] Since this porosity was not found in bead-on-plate welds made with adequate shielding, it was surmised that the porosity was due to contaminants in sheet laminations that had been opened up during edge preparation. In carbon-deoxidized molybdenum, the porosity is probably due to the carbon-oxygen reaction, whereas in powder-metallurgy molybdenum the porosity could be due to the high vapor pressure of MoO_3 at the melting point of molybdenum.[3] Weare, Monroe, and Martin[15] found no effect of the fusion-line porosity on weldment ductility in arc-cast carbon-deoxidized molybdenum. However, the presence of porosity in molybdenum welds is a sign of the presence of oxygen and should be avoided if possible.

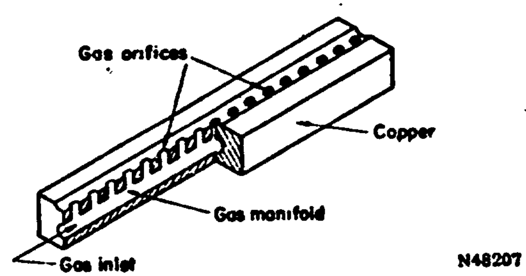
Tungsten contamination during tungsten-arc welding will lower the ductility of the welds.[15] Some persons believe that thoriated-tungsten electrodes should not be used because of their oxide content, which may contaminate the welds.[8] Thoriated-tungsten electrodes are generally



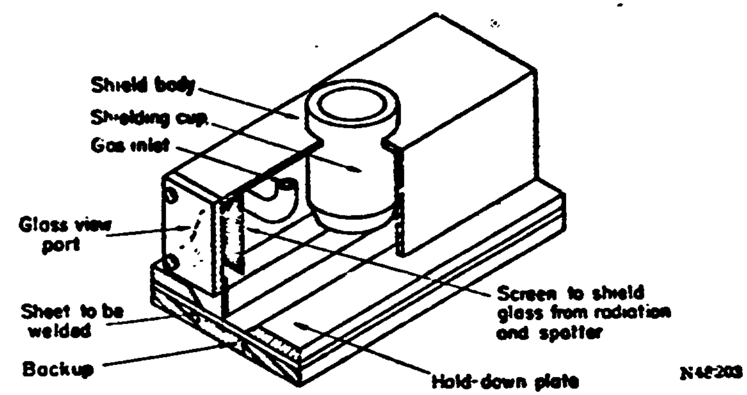
Diffused Flow, Gas Backup



Trailing and Leading Shield



Simple Flow, Gas Backup



Dragging Shield

FIGURE 13. TYPES OF SHIELDS AND GAS BACKUPS USED FOR WELDING MOLYBDENUM IN AIR

preferred, however, because of ease of arc starting, less tendency for electrode sticking to the work, and the extended current range in which they can operate without melting.

Several persons have attempted to improve the ductility of molybdenum welds by some postweld treatment. A stress relief of 1800 F for 1 hour in hydrogen has been used, but the effect of this treatment on the bend ductility of simple butt welds used for determining weld ductility has not been determined. Stress relief did lessen the degree of crater cracking experienced by Platte, and it is felt that such a stress relief is beneficial when complex structures are welded. Platte attempted to improve weldments embrittled by nitrogen by diffusing the nitrogen from the weld into the base plate.[20] However, he found that the slight improvement in ductility was not justified by the expense. He also attempted to polygonize the coarse weld metal by stressing the weld at elevated temperature.[21] These studies indicated that polygonization was not successful in improving weldment ductility. Platte, in a study of precipitates in molybdenum weld metal, indicated that it might be possible to improve the properties by a postweld heat treatment at 1200 C, but indicated the presence of boundary precipitates in material treated in this manner.[20] Perry, Spacil, and Wulff found that annealing low-carbon molybdenum in the temperature range 1950 to 2100 C (3542 to 3812 F) led to the formation of spheroidal oxide inclusions, which resulted in a low-strength, ductile material.[3] Many of these postweld heat treatments, with the exception of stress relieving, involve recrystallization of the base metal and thus a distinct lowering of the strength. Monroe and Martin[22] and Boam[23] mention the usefulness of a 400 F preheat to prevent cracking in the welding of complex structures of molybdenum.

Cold working of molybdenum is the only method of strengthening present molybdenum-base alloys. This also improves the bend ductility. Possible improvement of weld-metal ductility and strength would occur if welds were roll planished after welding.[24] This method consists of cold working the weld metal by rolling. Special equipment is available for this postweld treatment. This treatment would have to be carried out at an elevated temperature, possibly 1800 to 2000 F. Roll planishing, however, could not be used on complex structures.

Another possible method of improving weldment ductility would be the reduction of the weld-metal grain size. Battelle investigators[5] studied the effect on grain size of small additions of oxides to cast molybdenum. Castings containing some oxides did have smaller grains, but the effect on ductility was not determined. A similar method was attempted on a tungsten-arc weld in which tungsten carbide powder was added to the weld metal.[25] The tungsten carbide segregated at the root of the weld, where it decreased the weld grain size. Platte attempted to decrease the grain size by increasing the welding speed.[21] Increasing the speed decreased the weld-metal grain size only a slight amount and, at the highest speeds studied, retraction of the weld from the plate occurred. The effect on ductility is shown in

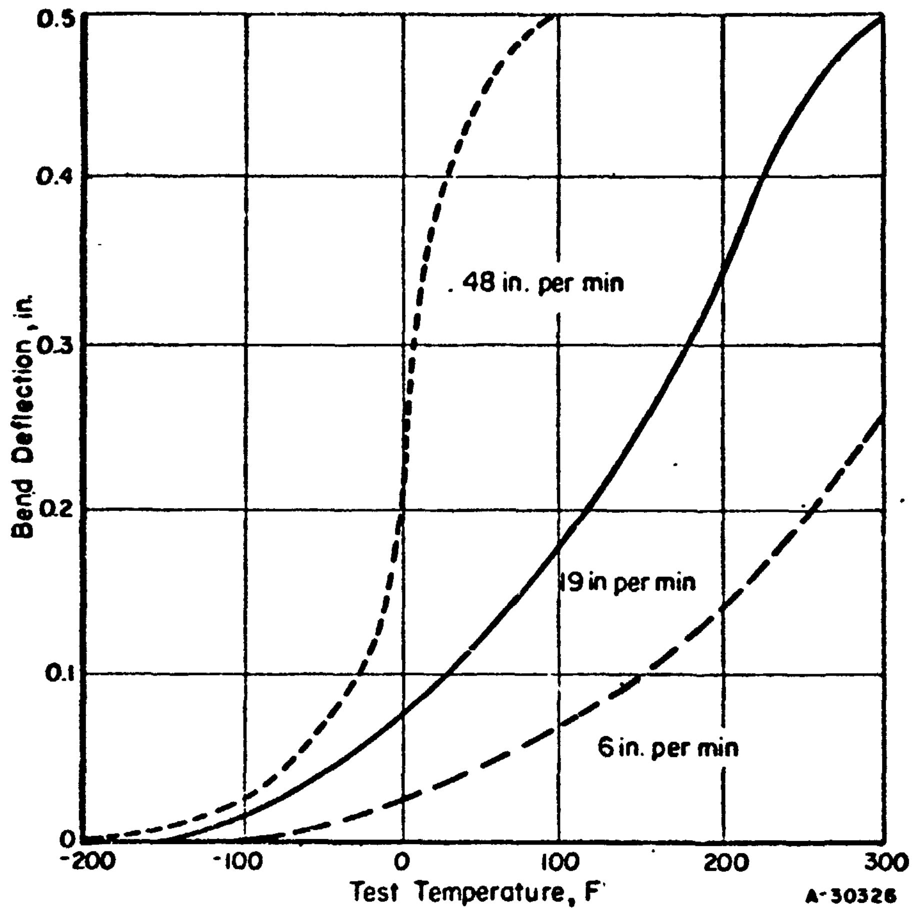


FIGURE 14. EFFECT OF TRAVEL SPEED ON BEND DUCTILITY OF WELDS IN MOLYBDENUM[21]

From bend tests at 0.0003 in./in./sec strain rate.

Figure 14. The temperature for brittle behavior was slightly affected; however, the temperature for ductile behavior was greatly lowered by increased weld speed. Because of the high melting point and good thermal conductivity of molybdenum, additional chilling of the weld probably has little effect on nucleation and grain growth.

Weare, Monroe, and Martin studied the consistency in weldment ductility of welds made in different lots of molybdenum containing nearly the same amount of carbon (0.015 to 0.021 per cent carbon).[15] The data obtained from a statistical analysis of this study are given in Table 2. It was found that significant differences in weldment ductility did exist in welds in different heats of arc-cast molybdenum. These data show that welds made outside the dry box using a standard shielding cup and gas backing were not so ductile, nor were their ductilities so consistent, as for welds made in a high-purity dry-box atmosphere. The most ductile welds were made in sheet from rolled sheet bar, whereas sheet in which welds were less ductile was made from forged sheet bar. Some of the least ductile welds were also made in the least ductile sheet. This sheet had a coarse grain structure and was not cross rolled. However, without complete knowledge of the fabrication procedures, definite conclusions could not be drawn regarding the effect of fabrication procedure on the ductility of molybdenum fusion weldments. Boam noted that weld cracking occasionally could be traced to poor yield from the ingot.[23]

TABLE 2. AVERAGE BEND ANGLE AND FACTORS FOR DETERMINING SIGNIFICANT DIFFERENCES FOR HEATS TESTED IN CONSISTENCY RUN[15]

		25 C[a]		75 C[a]		Average[b]	
Atmosphere	Rank	Heat	Avg Bend Angle, deg	Heat	Avg Bend Angle, deg	Heat	Avg Bend Angle, deg
Dry box	1	C23	64.0	C22	74.5	C23	69.0
	2	C22	60.8	C23	74.0	C22	67.6
	3	C21	44.7	C25	68.1	C21	55.8
	4	C24	44.5	C21	66.9	C24	55.3
	5	C25	38.0	C24	66.2	C25	53.0
	6	C26	37.6	C26	57.4	C26	47.5
Air, helium shield	1	C21	36.4	C21	67.9	C21	52.1
	2	C23	28.5	C23	58.7	C23	43.6
	3	C22	21.7	C22	57.7	C22	39.7
	4	C26	17.8	C25	51.2	C25	34.1
	5	C25	17.0	C26	40.8	C26	29.3
	6	C24	8.2	C24	31.0	C24	19.6

(a) Significant difference (probability level of risk, 5 per cent) 13.3 deg. Highly significant difference (probability level of risk, 1 per cent) 17.6 deg.

(b) Significant difference (probability level of risk, 5 per cent) 9.4 deg. Highly significant difference (probability level of risk, 1 per cent) 12.4 deg.

Although many persons have investigated and used the tungsten-arc process to weld molybdenum, there are few data available of any engineering significance. Most investigators used a bend test to study the ductility of weldments. Data obtained by different investigators are difficult to compare because of differences in testing procedures, notably strain rate. Some of the results obtained by these investigators are given in Table 3. Some investigators have determined the tensile strength of molybdenum fusion welds. Boam reported a weld tensile strength of 53,000 psi for a weld in wrought molybdenum possessing a 98,000-psi tensile strength.[23] The failure occurred in the heat-affected zone. Some tensile data obtained by Kearns for 0.061-inch-thick molybdenum-0.5 per cent titanium alloy tungsten-arc welds are given in Figure 15[27] and stress-rupture data are given in Figure 16.[26]

Weare, Monroe, and Martin studied the inert-gas-shielded consumable-electrode welding of molybdenum.[18] This process would eliminate tungsten contamination, and it was felt that a finer weld-metal grain size might result from the more rapid energy input available with this process. Poor arc stability and metal transfer were problems that required solution before any evaluation of the process could be made. It was found that coating the arc cathode with an emissive compound improved the arc stability. A good spray-type metal transfer was never obtained. Best results were obtained by welding in helium with direct-current straight polarity (electrode negative) with an emissive coating on the electrode. This study pointed out that notches or reduced cross-sectional areas will cause cracks to propagate because of the thermal stresses induced by welding. Because good arc stability and metal transfer were not obtained, no worthwhile comparisons could be made between consumable-electrode welds and tungsten-arc welds. Inert-gas-shielded consumable-electrode welding may be useful in joining heavier sections of molybdenum.

Goodman studied submerged-arc welding of molybdenum using commercial steel welding fluxes as the basis for additions of metals or oxides.[28] The welding was done in a nitrogen atmosphere preheated to 400 to 1000 F. Molybdenum probably reacted with oxides of the flux to produce molybdenum oxide. Considerable alloying was noted. No weldment properties were reported, but it is probable that the welds were extremely brittle.

A more recent process that has promise for joining molybdenum is the electron-beam welding process.[29] In this process, fusion welding is carried out in a high vacuum. Fusion is accomplished by bombardment of the joint by an electron beam. For this process, residual carbon would be the best deoxidant, since its reaction product with oxygen is gaseous. This should result in high-purity weld metal.

TABLE 3. BEND-TEST DATA FOR FUSION WELDS IN 0.062-INCH-THICK MOLYBDENUM

Molybdenum Alloy	Weld Shielding	Test Temperature, F	Deflection Rate, in./min	Strain Rate, in./in./sec	Punch Radius, in.	Radius of Bead, in.	Bend Angle, degrees	Elongation(a), per cent	Transition Temperature, F	Reference
Unalloyed (0.017%C)	Vacuum-purged dry box, high-purity atm	77	1	0.016	1/16	Not measured	64(b)	Not determined	Not determined	(15)
		167	1	0.016	1/16	Ditto	74(b)	Ditto	Ditto	(15)
Unalloyed (0.017%C)	Shielding cup, flowing tank He	77	1	0.016	1/16	-	28(b)	-	-	(15)
		167	1	0.016	1/16	-	56(b)	-	-	(15)
Unalloyed (0.020%C)	Vacuum-purged dry box, high-purity atm	77	1	0.016	1/16	-	70-90	-	-40	(17)
Ti-Neutralized (0.7%Ti, 0.002%C)	Vacuum-purged dry box, high-purity atm	77	1	0.016	1/16	-	6-90	-	-76	(17)
Mo-0.5%Ti (0.05%C)	Flow-purged dry box, welding-grade argon	120	0.1	0.0003	--	-	118	-	-240	(20)
		180	0.1	0.0003	--	-	70	-	-240	(20)
		-240	0.1	0.0003	--	-	0		-240	(20)
Mo-0.5%Ti (0.059%C)	Flow-purged dry box, high-purity atm	80	0.1	0.0003	--	-	118	-	-240	(20)
		0	0.1	0.0003	--	-	12	-	-240	(20)
		-240	0.1	0.0003	--	-	00	-	-240	(20)
Mo-0.5%Ti (0.021%C)	Vacuum-purged dry box	80	1/4	0.001	1/4	7/32	97	12.5	Not determined	(27)
		80	1/2	0.002	1/4	1/4-11/32	45-55	8.5-11	Ditto	(27)
		80	1	0.004	1/4	5/32-7-3/8	20-75	<8-16.5	-	(27)
		200	1	0.004	1/8	1/8-5/32	75-105	16.5-20	-	(27)
		200	1	0.004	1/16	1/8-5/16	90-105	9-20	-	(27)
		300	1	0.004	1/16	3/32-1/8	105	20-25	-	(27)

(a) Approximate for outermost fiber.
(b) Average values.

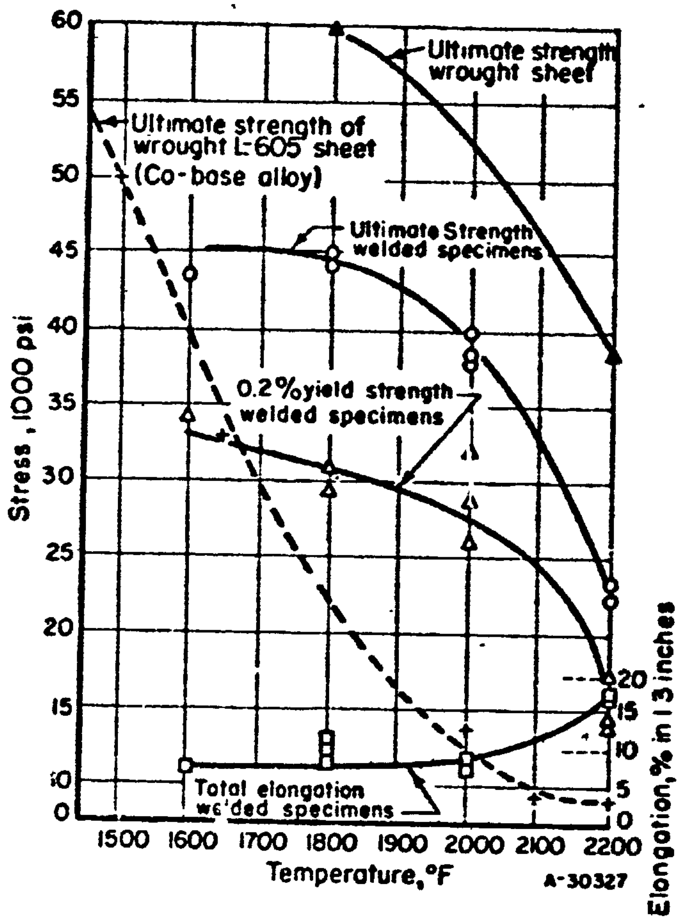
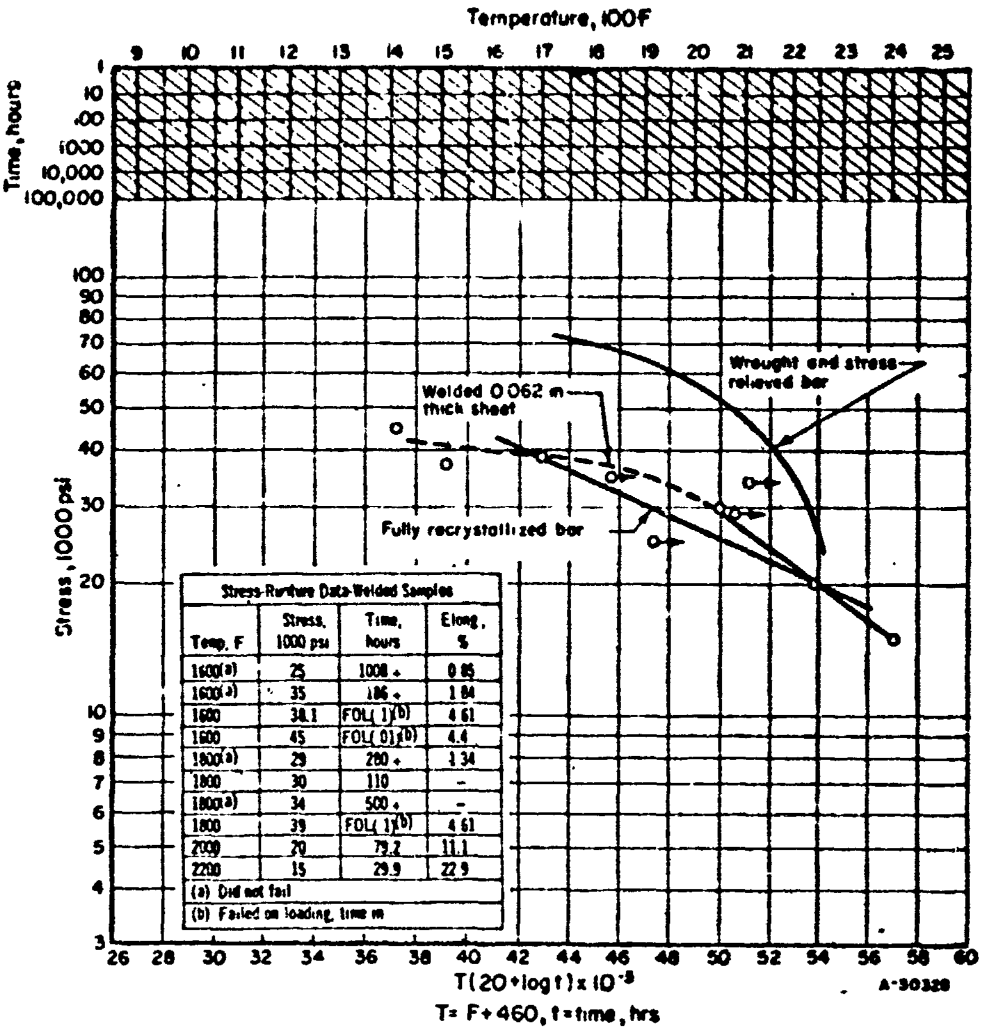


FIGURE 15. TENSILE PROPERTIES OF WELDED AND UNWELDED 0.062-INCH-THICK MOLYBDENUM – 0.5 PER CENT TITANIUM ALLOY SHEET[27]



Stress-Rupture Data-Welded Samples			
Temp, F	Stress, 1000 psi	Time, hours	Elong, %
1600(a)	25	1008+	0.85
1600(a)	35	186+	1.84
1600	38.1	FOL(1)(b)	4.61
1600	45	FOL(0)(b)	4.4
1800(a)	29	280+	1.34
1800	30	110	–
1800(a)	34	500+	–
1800	39	FOL(1)(b)	4.61
2000	20	79.2	11.1
2200	15	29.9	22.9
(a) Did not fail			
(b) Failed on loading, time in			

FIGURE 16. STRESS-RUPTURE STRENGTH OF MOLYBDENUM – 0.5 PER CENT TITANIUM ALLOY[26]

Resistance Welding

Spot welding has been used for several years to join molybdenum for electronic use. In these applications, the mechanical properties of the joints are of little importance. Spot welds in molybdenum are brittle and generally weak, and for this reason resistance welding is of little interest in producing structures of molybdenum. Flash welding has shown some promise in joining rods or bars of molybdenum. Spot welding will be discussed briefly and the results of flash-welding studies will be given in this section. Several investigators have made upset-butt welds using resistance-welding equipment, but, since these represent solid-state bonds, they will be discussed in a later section.

Molybdenum is difficult to resistance weld because of its high melting point and thermal conductivity. Spot-welded joints in molybdenum are brittle, and the notch found in all lap welds rules out spot or seam welding as a method of joining molybdenum structures where strength and some ductility are required. Extreme deformation of electrodes and sticking of the electrodes to molybdenum also are problems in spot welding molybdenum, although the latter has been alleviated by placing lead foil between the molybdenum and the copper electrodes.[35] Several investigators have joined molybdenum by placing nickel, tantalum, or some brazing alloy between the sheets of molybdenum being welded.[30,31,35] Resistance spot welding also is improved if projections are made on the two sheets being joined.[30] All joints made by these methods must be considered undesirable for structural uses. Tensile-shear strengths of molybdenum spot welds made by a condenser-discharge welder are given in Figure 17.[30]

Nippes and Chang[32,33] report some success in flash welding molybdenum rods. They showed fairly good bend ductility, but bend tests were carried out at extremely low strain rates. It was found that welds possessing some ductility could be made in air, argon, or hydrogen. Flash welds in arc-cast molybdenum made in air were found to be more ductile than welds made in an atmosphere of argon or hydrogen. This was attributed by Nippes and Chang to decarburization of the weld zone by reaction with oxygen. Weldment ductility was decreased by entrapped oxides at the interface, excessive upset, and carbide precipitation in the heat-affected zone. Some results of their work are shown in Figure 18. One important factor to keep in mind when flash welding is that the platen acceleration during welding should be as high as possible and the upset should be held in the critical range, which depends upon the size and shape of the parts being welded. This range was 0.10 to 0.21 inch for the rods flash welded in this study. Current requirements were two to three times those required for mild steel. Flash welding probably would have limited use in joining molybdenum components.

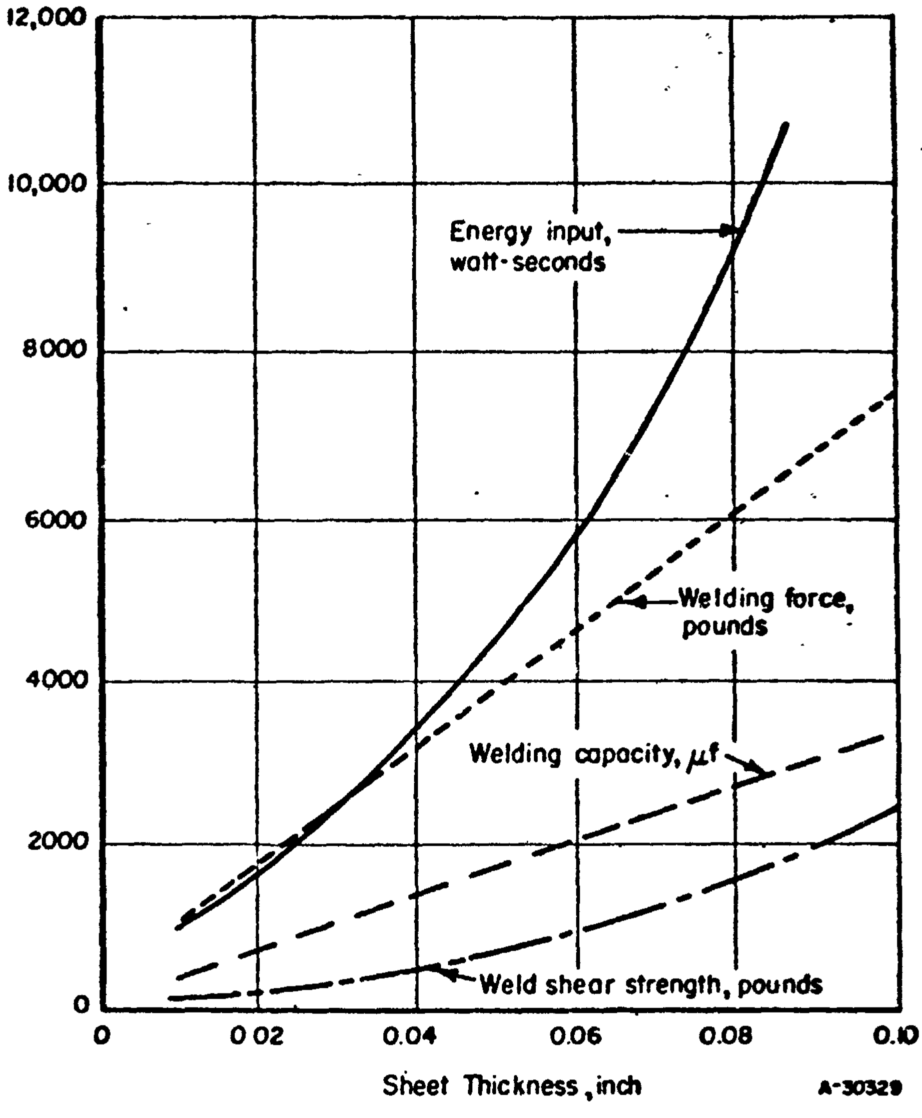


FIGURE 17. CONDITIONS USED FOR AND RESULTS OBTAINED IN SPOT WELDING MOLYBDENUM SHEET[30]

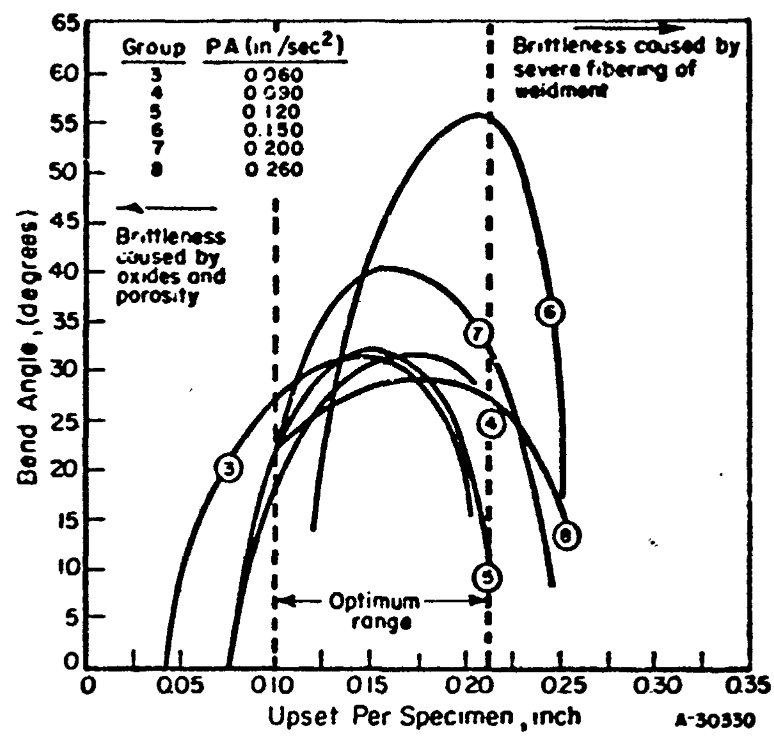


FIGURE 18. EFFECT OF UPSETTING CONDITIONS ON BEND ANGLE OF ARC-CAST-MOLYBDENUM FLASH WELDS (ALL WELDS MADE IN AIR)(32, 33)

Solid-State Welding

The brittleness of molybdenum fusion welds has caused some investigators to study solid-state welding. This method would eliminate the coarse grain structure and might prevent precipitation of oxides or carbides in the grain boundaries.

Moss studied the impact pressure welding of commercial molybdenum in hydrogen and in a vacuum.[34] He found that welds could be made at temperatures as low as 1274 F (690 C) but recommended using the highest temperature that can be used without recrystallizing the molybdenum. The use of a softer metal insert in the interface decreased the temperature and deformation required to produce a bond. Insert materials studied included: platinum-13 per cent rhodium, tantalum, powdered iron, austenitic stainless steel, nickel, columbium, and chromium plate. When intermetallics formed, brittle joints resulted. The best welds were made in dry hydrogen. Fair ductility at room temperature, and low strength were reported for pressure welds made in a vacuum. The data are of little value, because testing conditions and base-material properties were not reported. Room-temperature mechanical-property data reported by Moss for rod-type pressure welds made in a vacuum are:

Bend Test	Tensile Test
Breaking angle – 21 degrees	Yield point – 57,000 psi
	Ultimate tensile strength – 77,000 psi
	Elongation – 14 per cent
	Reduction of area – 11 per cent

Johnston, Udin, and Wulff carried out upset welding of molybdenum in hydrogen, chlorine, helium, carbon tetrachloride, or water.[35] Best results were obtained by welding under carbon tetrachloride or water. Lithium or sodium in the joint offered some improvement when welding under carbon tetrachloride. Some welds were produced having ductilities approaching that of the parent metal. These investigators found that the success of the process was based on control of three key metallurgical variables:

(1) Peak temperatures had to be carefully regulated to allow forging of the embrittled zone (recrystallized metal), but without excessive fusion at the interface.

(2) Time at temperature had to be minimized.

(3) Fast, extensive upset was required to insure adequate forging of the embrittled zone and render beneficial deformation.

Kearns, et al.,[36,37] found that ductile upset welds could be made in purified molybdenum, provided adequate shielding was provided during welding. The best results were achieved by welding in a high vacuum.

Recently, the ultrasonic welding of molybdenum has been studied.[38,39] Ultrasonic spot welds in molybdenum possess low tensile shear strength and no cross-tension strength. One group of investigators reports cracking of the molybdenum during welding at room temperature to be a serious problem.[38]

Brazing

The electronics industry has brazed molybdenum to itself and other metals for a number of years. These joints involved small parts that must be leak tight, but did not require high strengths. Present emphasis is on the use of molybdenum for structural parts that will operate at high temperatures. For this reason, only brazing alloys with melting points exceeding 1800 F will be discussed here. Brazing has been studied for joining molybdenum to itself and to join oxidation-resistant coatings to molybdenum. Monroe[40] made a survey of the brazing of molybdenum. He found the work done by Jacobson[41] and Dike[42] to be particularly valuable sources of material on brazing of molybdenum. Metallurgical considerations regarding brazing of molybdenum were given in a previous section.

Molybdenum has been brazed to itself and other metals using various filler metals. Some of the high-temperature filler metals are listed in Table 4. Not all alloys appear to be equally satisfactory under slightly differing conditions. Conflicting evaluations regarding the suitability of various filler metals for brazing molybdenum in a vacuum or hydrogen atmosphere are not uncommon.

Satisfactory brazed joints in molybdenum have been made using all common brazing processes. Discussion of these processes will deal with factors affecting the selection of the best process for a given application. Before any brazing operation can be carried out, the molybdenum surfaces must be cleaned, using one of the procedures mentioned in the section on cleaning.

Furnace brazing of molybdenum assemblies can be carried out in inert or hydrogen atmospheres or in a vacuum. When using hydrogen atmospheres, only moderately low dew points are required for unalloyed molybdenum. According to Chang,[43] above 600 F (315 C), hydrogen with a dew point of 80 F (27 C) will reduce molybdenum dioxide. However, when brazing molybdenum-titanium alloys, the dew-point requirement is -100 F (-73 C) at 2200 F (1205 C) to prevent formation of titanium dioxide. Furnace brazing has the advantage of being adaptable to large and complex parts. Disadvantages are limited temperature range and relatively low heating

TABLE 4. HIGH-TEMPERATURE BRAZING ALLOYS FOR MOLYBDENUM

Alloy Name	Composition, per cent	Liquidus, F
	Pure Metals	
Copper	100 Cu	1980
Nickel	100 Ni	2650
Palladium	100 Pd	2860
Platinum	100 Pt	3225
	Nickel Base	
Wall Colmonoy No. 6	78Ni-18Cr-4B	1950
Nickel-titanium	84Ni-16Ti	2350
Hastelloy C	57Ni-17Mo-16Cr-6Fe-4W	2380
Monel	67Ni-30Cu	2460
Inconel	80Ni-14Cr-6Fe	2540
	Iron Base	
18-8 stainless steel	18Cr-8Ni-Bal. Fe	2600
25-20 stainless steel	25Cr-20Ni-Bal. Fe	2650
	Cobalt Base	
Haynes Alloy 21	54Co-27Cr-6Mo-3Ni	2550
Haynes Alloy 25	55Co-20Cr-15W-10Ni	2600
	Columbium Base	
Columbium-nickel	52Nb-48Ni	2175
	Palladium Base	
Palladium-aluminum	93Pd-7Al	2150
Palladium-nickel	53Pd-47Ni	2200
Ditto	60Pd-40Ni	2300
Palladium copper	60Pd-40Cu	2200
Ditto	65Pd-35Cu	2300
"	70Pd-30Cu	2400
Palladium-silver	50Pd-50Ag	2400
Ditto	60Pd-40Ag	2500
Palladium-iron	70Pd-30Fe	2400
Ditto	50Pd-50Fe	2400
	Molybdenum Base	
Molybdenum-boride	Mo-B eutectic	3450
Molybdenum-reuthenium	Mo-Ru	3450

rates, which may result in recrystallization of the molybdenum. Experimental furnace-brazed molybdenum assemblies weighing up to 50 pounds have been made successfully.

Oxyacetylene-torch brazing can be used to join molybdenum. Commercial fluxes suitable for use with silver-base and copper-base alloys can be used. Jacobson and Martin developed fluxes with melting points up to 2600 F (1427 C).[41] Fair protection was offered for brazing molybdenum in the temperature range 800 to 2600 F (427 to 1427 C) by a flux containing 50 per cent "Eutector 189" and 50 per cent CaF_2 mixed with alcohol and used in conjunction with a precoating of "Handy Flux". "Eutector 189" is a commercial borate-base brazing flux that is active in the range 1400 to 2000 F. "Handy Flux" is silver-soldering flux that melts at 800 F and is active up to 1600 F. The melting point of calcium fluoride is 2480 F. Additional work is felt necessary to develop completely satisfactory fluxes for brazing alloys melting above 2000 F (1093 C). The advantages of torch brazing are the availability of the necessary equipment, versatility, and simplicity. Disadvantages are inadequate fluxes for high temperatures, possible flux entrapment, and relative inefficiency in production.

Induction brazing, which provides fast and reliable heating cycles, has a substantial background of usage for electronic components. The high investment required for equipment generally limits its use to production items and, to some extent, to small or simple shapes. This process is easily adapted to brazing in vacuum or protective atmospheres.

Resistance brazing also can be used for molybdenum parts, but the shape and size of components that can be brazed this way are limited by the available sizes of resistance-heating equipment.

The major current uses of brazed molybdenum components have not required extensive compilations of property data. Future use in high-temperature structures, however, will require more knowledge of the mechanical properties of molybdenum brazes and studies of the properties that determine suitability for operation in various environments.

Brazed joints are generally designed for shear loading because preferred joint designs usually call for some overlap to facilitate the brazing operation. Exact determination of the shear strength of brazed joints at room temperature has not been possible because of the notch sensitivity of molybdenum. However, the results of short-time tensile tests at 1800 F (982 C) that have been published[41] indicated that the braze shear strength could be higher or lower than the tensile strength of the filler metal. This behavior is common for many brazed materials. Where diffusion of molybdenum into the braze occurs (typical of nickel-base alloys), a strengthening effect was observed. Strengths lower than those of the filler metals are probably caused by the formation of brittle intermetallics at the bond line. The highest braze shear strength was approximately 19,000 psi at 1800 F when using Inconel as the brazing alloy. Similar specimens brazed with

Inconel had a 100-hour stress-rupture strength of 5000 psi at 1800 F. Some shear and stress-rupture data are given in Table 5 and Figure 19, respectively.

TABLE 5. SHEAR STRENGTHS OF BRAZED JOINTS IN MOLYBDENUM

Brazing Alloy	Test Temperature, F	Type of Joint	Shear Strength, psi
Inconel	1800	Slotted	18,800
Haynes Alloy 25	1800	Slotted	14,250
Monel	1800	Slotted	12,750
Hastelloy C	1800	Slotted	12,000
Haynes Stellite 21	1800	Slotted	12,000
53Pd-47Ni	1800	Slotted	9,400
60Pd-40Cu	1800	Slotted	6,400
60Pd-40Ag	1800	Slotted	4,500
60Pd-40Ni	1500	Single lap	15,900-18,100
65Pd-35Cu	Room	Ditto	29,000-33,100
	1500	"	5,800-9,400
70Pd-30Cu	700	"	14,100-16,200
	1000	"	14,800-17,000
93Pd-7Al	1500	"	13,200-13,500

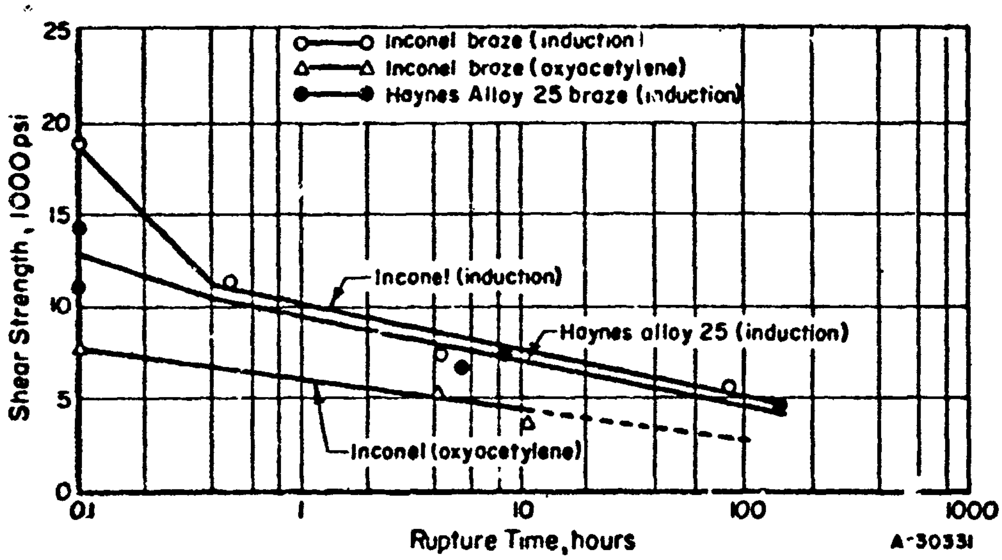


FIGURE 19. STRESS-RUPTURE CURVES AT 1800 F FOR BRAZES MADE WITH INCONEL AND HAYNES ALLOY 25[41]

Studies of the tensile strength of vacuum-brazed joints[42] 0.001 to 0.002 inch thick showed strengths as high as 20,000 psi at 1800 F (982 C) (see Table 6). Three alloys, 84 per cent nickel-16 per cent titanium, 52 per cent columbium-48 per cent nickel, and 50 per cent iron-50 per cent palladium, were subjected to 24-hour treatment at 1800 F to determine the effects of operation at this temperature on joint strength at 1800 F. The strength of the iron-palladium-alloy brazes was reduced to about one-third of its previous strength, but the strength of the other brazes was not affected.

TABLE 6. TENSILE STRENGTHS OF BRAZED BUTT JOINTS IN MOLYBDENUM

Brazing Alloy	Test Temperature, F	Tensile Strength, psi
70Pu-30Cu	1500	25,200-34,800
	1800	9,700-13,900
	2000	6,900
84Ni-16Ti	Room	26,200-27,800
	Room[a]	22,200-28,400
	1800	17,600-18,100
	1800[a]	17,300-18,300
52Nb-48Ni	Room	21,700
	Room[a]	25,500-39,700
	1800	18,900
	1800[a]	17,300-19,900
50Pd-50Fe	Room	49,400
	Room[a]	43,500
	1800	17,300
	1800[a]	6,600-7,150

(a) Heated for 24 hours at 1800 F in vacuum prior to testing.

A recent study has been made of brazed joints in the molybdenum-0.5 per cent titanium alloy.[44] The joints were furnace brazed in a hydrogen atmosphere. Palladium-base brazing alloys were found to be the most promising for high-temperature service.

In addition to strength, the braze properties that are most likely to determine the suitability of using a given alloy or procedure with molybdenum are those properties influenced by the service environment. Vacuum-tube applications require the use of brazing alloys that do not contain elements that volatilize easily or outgas excessively; therefore, alloys

containing cadmium and zinc and the use of fluxes are not recommended. Brazes in parts subjected to oxidizing environments must be oxidation resistant or must not interfere with the application of oxidation-resistant coatings. In the first instance, most of the high-temperature alloys are generally suitable, whereas the latter case may require brazing alloys with very high melting temperatures to allow coating with silicides or other ceramic coatings.

The behavior of brazed parts in liquid metals, fused salts, or glasses where molybdenum has excellent corrosion resistance is difficult to predict. Not only must the braze filler metal have good corrosion resistance, but there should not be any corrosive effects caused by the presence of a bimetallic system. Effects such as mass transfer in liquid-metal systems are generally not severe except in polythermal systems.

BIBLIOGRAPHY

The bibliography lists all the source material used in the writing of this report. References are found under the section headings to which they have the greatest application. Many references contain information applicable to more than one subject heading.

Metallurgical Considerations

(1) Case, S. L., "Summary Report on a Metallurgical Study of Molybdenum", Battelle Memorial Institute Report to the Office of Naval Research, Navy Department (Contract No. N9onr 82100), October 15, 1954.

(2) Climax Molybdenum Company, "Arc-Cast Molybdenum and Its Alloys" (1955).

(3) Perry, T., Spacil, H. S., and Wulff, J., "Effect of Oxygen on Welding and Brazing Molybdenum", Welding Journal, Research Supplement, 33 (9), 442s-448s (1954).

(4) Semchyshen, M., "Development and Properties of Arc-Cast Molybdenum-Base Alloys", The Metal Molybdenum, American Society for Metals, Cleveland, Ohio, 281-329 (1958).

(5) Jaffe, R. I., "Powder Metallurgy Molybdenum-Base Alloys", The Metal Molybdenum, American Society for Metals, Cleveland, Ohio, 330-364 (1958).

(6) Mikol, E. P., "The Thermal Conductivity of Molybdenum Over the Temperature Range 100-2100 F", ORNL-1131, February 28, 1952.

(7) Olds, L. E., and Fisher, R. B., "A Metallurgical Study of Molybdenum", Battelle Memorial Institute Report to the Office of Naval Research (Contract No. N9onr-82100), October 31, 1953.

(8) Northcott, L., Molybdenum, Academic Press, New York (1956).

Testing of Molybdenum Joints

(9) Bechtold, J. H., and Wessel, E. T., "Ductile-to-Brittle Transition in Molybdenum", The Metal Molybdenum, American Society for Metals, Cleveland, Ohio, 241-261 (1958).

Cleaning of Molybdenum

(10) "Found Deoxidizing Process to Clean Molybdenum for Welding", Western Metal, 15 (12), 61-62 (1957).

Fusion Welding of Molybdenum

(11) Platte, W. N., "Welding of Molybdenum", The Metal Molybdenum, American Society for Metals, Cleveland, Ohio, 151-191 (1958).

(12) Platte, W. N., United States Patent No. 2,839,819, June 24, 1958.

(13) Platte, W. N., "Influence of Oxygen on the Soundness and Ductility of Molybdenum Welds", Welding Journal, Research Supplement, 35 (8), 369s-381s (1956).

(14) Platte, W. N., "Effect of Nitrogen on the Soundness and Ductility of Molybdenum Welds", Welding Journal, Research Supplement, 36 (6), 301s-306s (1957).

(15) Weare, N. E., Monroe, R. E., and Martin, D. C., "Ductility of Tungsten-Arc Welds in Molybdenum", Welding Journal, Research Supplement, 36 (6), 291s-300s (1957).

(16) Gorman, E. F., "Inert Gases for Controlled-Atmosphere Processes", Welding Journal, 37 (9), 882-889 (1958).

(17) Monroe, E. F., Weare, N. E., and Martin, D. C., "Fabrication and Welding of Arc-Cast Molybdenum", Welding Journal, Research Supplement, 35 (10), 488s-498s (1956).

(18) Weare, N. E., Monroe R. E., and Martin, D. C., "Inert-Gas-Shielded Consumable-Electrode Welding of Molybdenum", Welding Journal, Research Supplement, 37 (3), 118s-124s (1958).

(19) Weare, N. E., and Monroe, R. E., "Controlled Atmosphere Arc-Welding", Welding Journal, 37 (12), 1169-1175 (1958).

(20) Platte, W. N., "Joining of Molybdenum", WADC Technical Report 54-17, Parts 1, 2, and 3, November, 1956.
[illegible]

(21) Platte, W. N., "Joining of Molybdenum", WADC Technical Report 57-309, August, 1957.
[illegible]

(22) Monroe, R. E., and Martin, D. C., "Welding of Molybdenum Heat Exchangers", Welding Journal, 35 (12), 1222-1225 (1956).

(23) Boam, W. M., "Jet Engine Push Welded Molybdenum Study", Iron Age, 170, 145-148 (July 10, 1952).

(24) Meredith, H. L., and Russel, B. R., "Roll Planishing Improves Weld-Joint Efficiency and Quality", Welding Journal, 36 (2), 113-117 (1957).

(25) Weare, N. E., unpublished data.

(26) Kearns, W. H., private communication.

(27) Kulju, K. M., and Kearns, W. H., "Welding of Molybdenum Alloy Sheet", Welding Journal, Research Supplement, 37 (10), 440s-444s (1958).

(28) Goodman, L. S., "Arc Welding of Molybdenum", Welding Journal, 29 (1), 37-44 (1950).

(29) Wyman, W. L., "High-Vacuum Electron-Beam Fusion Welding", Welding Journal, Research Supplement, 37 (2), 49s-53s (1958).

Resistance Welding of Molybdenum

(30) Heuschkel, J., "Welding High Purity Molybdenum", Iron Age, 162, 87-89 (December 16, 1948).

(31) Chelius, J., "How to Fabricate Molybdenum", Materials and Methods, 32 (7), 45-48 (1950).

(32) Nippes, E. F., and Chang, W. H., "The Flash Welding of Commercial Molybdenum - Part I", Welding Journal, Research Supplement, 34 (3), 132s-140s (1955).

(33) Nippes, E. F., and Chang, W. H., "The Flash Welding of Commercial Molybdenum - Part II", Welding Journal, Research Supplement, 34 (5), 251s-264s (1955).

Solid-State Welding of Molybdenum

(34) Moss, A. R., "The Pressure Welding of Molybdenum", Journal of the Institute of Metals, 82, 374-378 (1954).

(35) Johnston, J. H., Udin, H., and Wulff, J., "Joining of Molybdenum", Welding Journal, Research Supplement, 33 (9), 449s-458s (1954).

(36) Kearns, W. H., Goodwin, H. B., Martin, D. C., and Voldrich, C. B., "Welding of Molybdenum", BMI-703, September 1, 1951.

(37) Kearns, W. H., Eichen, E., Martin, D. C., and Voldrich, C. B., "The Effect of Purification in Welds in Molybdenum", BMI-788, December 1, 1952.

(38) Weare, N. E., Monroe, R. E., Antonevich, J. N., and Martin, D. C., "Research and Development of Procedures for the Joining of Similar and Dissimilar Heat-Resisting Alloys by Ultrasonic Welding", WADC Technical Report 58-479, July, 1958.
AD-207323

(39) Jones, J. B., "Ultrasonic Welding of High-Temperature and Corrosion-Resistant Material", paper presented at joint meeting of Washington, D. C., Chapters of the American Society for Metals and the American Welding Society, December 9, 1957.

Brazing of Molybdenum

(40) Monroe, R. E., "Brazing of Molybdenum", The Metal Molybdenum, American Society for Metals, Cleveland, Ohio, 192-198 (1958).

(41) Jacobson, M. I., and Martin, D. C., "Brazing Molybdenum for High Temperature Service", Welding Journal, Research Supplement, 34 (2), 65s-74s (1955).

(42) Dike, K. C., "Evaluation of Alloys for Vacuum Brazing of Sintered Wrought Molybdenum for Elevated Temperature Applications", National Advisory Committee for Aeronautics Technical Note 3148, May, 1954.

(43) Chang, W. H., "A Dew Point Temperatures Diagram for Metal - Metal Oxide Equilibrium in Hydrogen Atmospheres", Welding Journal, Research Supplement, 35 (7), 622s-624s (1956).

(44) Hoppin, G. S., III, "Brazing of Molybdenum", paper presented at the ASM Molybdenum Fabrication Conference in Los Angeles, May 8, 1958.

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